Pressure effects on maghemite (γ-Fe$_2$O$_3$) with an ordered vacancy sub-lattice

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The behaviour of magnetite Fe_3O_4 at high pressure has been tackled quite extensively in recent years in an effort to eluci-date the magnetic-electronic state and structural characteristics of the high-pressure phase [1]. Maghemite (γ-Fe$_2$O$_3$), the fully oxidised structural analogue of magnetite Fe_3O_4, is both of geophysical significance and of crucial importance to the magnetic read-write recording industries. In this study the behaviour of a well-characterised sample of maghemite, in which there is evidence of vacancy ordering [2], has been investi-gated under quasi-hydrostatic conditions in a diamond-anvil cell at pressures up to ~30 GPa using synchrotron X-ray diffraction (beamline XRD1, ELETTRA).

In maghemite iron is trivalent in the spinel lattice and a prepon-derance of ordered or disordered vacancies (perhaps partially occupied by impurity atoms) occurs, to ensure charge compen-sation. Our sample has vacancies in an ordered array as deduced from the superstructure peaks in the diffraction pattern [2]. The original ordered vacancy structure is main-tained upon pressurising to ~17 GPa. This is also the onset transformation pressure from maghemite to a new structural phase, ascribed to hematite (α-Fe$_2$O$_3$). Maghemite (and vacancy super-structure) phase signatures coexist with the new structural phase up to ~25 GPa. Radical changes occur to the original maghemite vacancy superstructure in this regime of phase coexistence. The transformation to the new structural phase of Fe_2O_3 is completed at ~27 GPa. This is similar to the transition pressures reported in a previous ^{57}Fe Mössbauer pressure study of well crystal-lized maghemite [3] and for annealed bulk γ-Fe$_2$O$_3$ [4]. The pressure-induced transfor-mation is irreversible and upon decompression the high pressure phase is preserved to ambient conditions.

The bulk modulus for the maghemite and the hematite high-pressure phase have been extracted from the *P-V* data.

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Observation of the second percolation threshold during recrystallization in amorphous pyrochlore

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Irradiating a material with energetic ions or doping it with radioactive elements results in dramatic changes of its physical properties. Natural pyrochlores ($A_2B_2O_7$), containing uranium and thorium impurities, are a good example of this, under-going a crystalline to amorphous transformation over geologic periods of time. Amorphous pyrochlore can fully recover its original crystalline order when subject to temperatures in excess of ~ 400 ° C. During amorphization and recrystallization, the system proceeds through several stages where crystalline regions (amorphous regions) go from being a majority (minority) phase to a minority (majority) phase. Such a system can be described within the percolation theory, and some of its properties explained following this formalism. At the heart of the theory lies the result that a system starts to behave qualitatively differ-ently once the percolating cluster is formed, signalling the onset of macroscopic correlations and overall change of system behaviour. Thus, two critical thresholds are expected during amorphization. The first one relates to the amorphous fraction, p1, for which the amorphous phase starts to percolate, whereas the second one corresponds to the amorphous fraction, p2, for which the crystalline phase stops percolating [1].

During recrystallization, a similar behaviour is expected.

Using x-ray diffraction, both the amorphous fraction and the cell parameter (Fd-3m) of the (nano)crystalline phase have been studied as a function of annealing temperature and time. Interestingly, lattice swelling of the nucleated crystalline regions is found to be fully released when the amorphous content decreases below 70%. This critical value matches perfectly well the prediction of the percolation theory for the second perco-lation point, p2, i.e., when crystalline regions start percolating during recrystallization (or stop percolating during amorphiza-tion).

These results provide with the first experimental observation of the second percolation threshold in a self-amorphized system. Results will be compared to previous studies on the case system $ZrSiO_4$ [2].

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